

# Phase transitions in simple and not so simple binary fluids

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**Abstract.** Compared to pure fluids, binary mixtures display a very diverse phase behavior, which depends sensitively on the parameters of the microscopic potential. Here we investigate the phase diagrams of simple model mixtures by use of a microscopic implementation of the renormalization group technique. First, we consider a symmetric mixture with attractive interactions, possibly relevant for describing fluids of molecules with internal degrees of freedom. Despite the simplicity of the model, slightly tuning the strength of the interactions between unlike species drastically changes the topology of the phase boundary, forcing or inhibiting demixing, and brings about several interesting features such as double critical points, tricritical points, and coexistence domains enclosing “islands” of homogeneous, mixed fluid. Homogeneous phase separation in mixtures can be driven also by purely repulsive interactions. As an example, we consider a model of soft particles which has been adopted to describe binary polymer solutions. This is shown to display demixing (fluid-fluid) transition at sufficiently high density. The nature and the physical properties of the corresponding phase transition are investigated.

The phase diagram of binary mixtures may show several transition lines, usually related to the physically different processes of demixing and liquid-vapor phase separation[1]. While the ordinary liquid-vapor phase transition is driven by the presence of attractive interactions, demixing may be occur also in purely repulsive fluids and even in strongly asymmetric, athermal (i.e. hard-core) systems. However, inspecting the composition of the phases at coexistence generally reveals a more structured scenario where both density and composition of the phase-separated fluids differ. Even in rare-gas mixtures, like the Ne-Kr system, the character of the transition can change from liquid-vapor at low pressure to mainly mixing-demixing at high pressure. This behavior requires a generalization of the concept of *order parameter*, allowing for linear combinations of density and concentration fluctuations: By moving along a critical line the nature of the order parameter, i.e. the weights of density and concentration fluctuations in the linear combination, smoothly changes signaling the change in the physical character of the transition. As a result, an ample variety of phase diagram topologies are possible in mixtures, and it is not surprising that small changes in the interaction parameters may have a crucial effect in determining important physical properties of the system, like the miscibility of two fluids at given pressure conditions.

In ordinary simple fluids, this sensitivity of the phase diagram to small changes in the interaction has not attracted much interest in the past, because we have little

possibility to affect the form of the interaction at the molecular level. However, a considerably richer scenario opens up in the framework of complex fluids. If the constituents of our mixtures are polymers, colloids or micelles, their mutual interaction is mediated by the solvent and then it depends on several properties which may be suitably modified, like polymer-chain lengths or salt concentration. It is therefore important to investigate how (small) changes in the interparticle potentials affect the global phase diagram and the structure of the mixture and whether it is possible to switch from one topology of the phase diagram to another by simply acting on the form of the effective interactions: physically this means that by small changes in the properties of the solvent we may “turn on” strong concentration fluctuations in the system, driving mixing or demixing.

Liquid-state theory offers several methods which allow the investigation of this problem[2]. A classical approach, which has been widely exploited in the past, is to resort to mean field theory (MFT) which has the considerable advantage to require very modest (if any) computational effort and to provide the full phase diagram of the model. However, the main drawbacks of MFT are the complete neglect of fluctuations, extremely relevant close to phase transitions, and the insensitivity to the *shape* of the interactions, which are known to play an important role in complex fluids [3]. A more sophisticated route to the theoretical investigation of phase diagrams is represented by the integral equation approach. This method is designed to study correlation functions and by now the best integral equations (the modified hypernetted chain or the Rogers-Young equations) provide a remarkably accurate representation of the structure of the model. Thermodynamics instead is obtained via the use of sum rules, but the resulting phase diagram often depends on the chosen route and suffers from a lack of convergence of the theory in the critical region, casting doubts on the accuracy of the method. The most reliable method to investigate phase coexistence in fluids is probably the Gibbs ensemble Monte Carlo method which proved quite successful in several different situations. However, simulations are rather time consuming, mainly because they provide information on a single thermodynamic state of the system. The possibility of mapping a large portion of the phase diagram is therefore hindered by the computational burden.

In this work, we present an investigation of the phase diagram of few simple models of binary mixtures by use of the Hierarchical Reference Theory of Fluids (HRT)[4], a method explicitly devised for studying the thermodynamics of liquids and gases which allows for the development of long-range fluctuations and consistently enforces the convexity of the free energy. The method is based on a splitting of the interaction in a repulsive-core part, treated as a reference system, and a “long-range” tail which is supposed to drive possible phase transitions. The effects on the thermodynamics of the long-range part are then introduced in the free energy recursively, starting from short wavelengths in a way which resembles the renormalization group strategy. HRT is especially useful to determine the phase boundaries and the equation of state of microscopic models where energy driven phase transitions are at play. It has been tested both in fluid and lattice systems, and accurate results have been obtained. A generalization to mixtures has been already numerically implemented both for lattice and off-lattice systems[5]. Here we discuss the phase diagram of a symmetric mixture when the ratio  $\Delta$  between the unlike and the like attractive interactions, is varied. The interparticle interactions  $w_{ij}(r)$  were modelled by a hard-core Yukawa (HCY) potential such that  $w_{ij}(r) = +\infty$  for  $r < \sigma$  and  $w_{ij}(r) = -\epsilon_{ij} \exp[-z(r - \sigma)]/r$  for  $r > \sigma$ , where  $i, j$  refer to the particle

species,  $\epsilon_{11} = \epsilon_{22}$ ,  $\epsilon_{12} = \Delta\epsilon_{11}$ ,  $\sigma$  is the particle diameter, and  $z$  is the inverse-range parameter, which we fixed at  $z = 1.8\sigma^{-1}$ . Full details regarding the computations will be soon available[6]. A similar model has been already studied by Monte Carlo methods[7]. This system offers an interesting example of competition between liquid-vapor and mixing-demixing transitions. As it can be appreciated from Fig. 1, an increase by just 10% of the unlike interaction  $\Delta$  leads to the formation of a stable mixed phase at liquid density and equimolar concentration. While for  $\Delta = 0.6$  the two fluids are miscible only in the gas phase, for  $\Delta = 0.67$ , at the same temperature, the two fluids mix also in the liquid region, i.e. at density up to  $\rho\sigma^3 \sim 0.5$ . In such a hypothetical system, by slightly tuning the interaction we may therefore inhibit demixing at high pressures. Criticality in this symmetric binary mixture presents a rich variety of different behaviors. For instance, at  $\Delta = 0.67$ , up to six critical points are present for each temperature in a small range below  $T^* = 1.03$ . Well above this characteristic temperature the system displays an ordinary consolute critical point which then turns to a tricritical point (an artifact due to the symmetry of the model). Below  $T^*$  one pair of (liquid-vapor) critical points merges, giving rise to a double critical point and then disappear. The remaining four critical points then merge in pairs (at  $T^* \sim 1.0235$ ) leaving an “island” in the density-concentration plane where the mixed liquid is stable. On further lowering the temperature, this one-phase domain shrinks, until it is eventually swallowed by the coexistence region. The phase diagram in the  $(\rho, T)$  plane at equimolar concentration is shown in Fig. 2.

Up to now we analyzed mixtures where phase transitions are driven by attractive potentials. However, colloidal suspensions are often characterized by purely repulsive interactions[8] and we may inquire whether also in this case the topology of the phase diagram depends on the details of the interaction. Some sensitivity on the specific form of the interaction in these systems has been already conjectured regarding the freezing transition[9]. We have investigated, by means of HRT, the gaussian-core model (GCM), whose interparticle potential has the form:

$$\beta v(r) = \epsilon \exp(-r^2/\sigma^2) \quad (1)$$

which has been proposed as an effective model for dilute and semi-dilute polymer solutions[10]. Here the interaction is purely repulsive and has entropic origin, being due to the self-avoidance of the polymer coils. The strength of the interaction depends on the number of monomers in the polymer. A characteristic feature of this model is the allowance of full overlap between “particles”. This apparently unphysical feature originates from the fact that in the effective model considered, a particle just represents the center of mass of the polymer, i.e. a geometric point and not a physical particle. No phase transition between homogeneous phases is observed in this model[11]. A two-component system of gaussian-core “molecules” has also been investigated both when the unlike interaction  $\epsilon_{12}$  is larger than the like ones  $\epsilon_{11} = \epsilon_{22}$  and in the opposite case[12, 13]. Note that in this model with purely repulsive interactions the liquid vapor transition does not occur, and in order to trigger the demixing transition positive non additivity in the core radii combination rule would be required if  $\Delta \equiv \epsilon_{12}/\epsilon_{11} < 1$ .

HRT appears particularly suitable for treating this class of effective interactions because it has been shown[14, 11] that the momentum dependence of the partial structure factors is well represented by the simple mean field approximation in a large portion of the phase diagram. This is of great help in devising the closure relation necessary to write the formally exact HRT equation in a manageable form. In Fig.3 (left panel) we report the density-concentration phase diagram of the GCM for few

choices of the interaction parameters, compared with the results obtained by MFT and HNC equation[12]. We remark that, for given  $\Delta$ , the MFT phase boundaries for different interaction strengths  $\epsilon_{11}$  collapse into the same curve when plotted in the units used in the figure[12], while this is not the case with either HNC or HRT. However, even according to these theories the changes induced by a significant increase in the interaction are just quantitative, while the overall topology of the phase diagram remains unaltered. When the strength of the unlike interaction grows, HRT pushes the phase boundary to higher densities with respect to HNC. A remarkable flattening of the phase boundaries is also predicted by HRT. Actually, the HRT binodals reported in the figure show portions that are completely straight, but this is due to the finite density mesh used in the computation. This applies also to the small jumps in the form of the binodals.

Accurate Monte Carlo simulations on this model may be useful to resolve the discrepancy between the two approaches. A snapshot of correlations is reported in the left panel where some clustering of the minority species, due to the softness of the repulsive interaction, can be seen close to the demixing transition[12].

The effective hamiltonian approach to complex fluids is intimately related to the possibility of tracing out degrees of freedom. However, we point out that in the class of models characterized by soft interactions this powerful technique, which is at the very basis of the concept of depletion interactions, may lead to unphysical results. As an example, we consider the gaussian-core mixture where an accurate free energy functional has been already introduced[11, 14, 13]. If we “freeze” the degrees of freedom of the  $N_1$  particles of species ‘1’ in a given, arbitrary, configuration  $\{\mathbf{R}_i\}$ , the free energy functional of the gas of particles ‘2’ in this inhomogeneous external potential can be accurately represented in mean-field approximation:

$$F[\rho(\mathbf{r})] = F_{id}[\rho(\mathbf{r})] + \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) v_{22}(\mathbf{r}_1 - \mathbf{r}_2) + \sum_i \int d\mathbf{r} v_{12}(\mathbf{r} - \mathbf{R}_i) \rho(\mathbf{r}) \quad (2)$$

This functional must be minimized in order to obtain the actual density profile  $\rho(\mathbf{r})$  of particles ‘2’ subject to the number conservation constraint  $\int d\mathbf{r} \rho(\mathbf{r}) = N_2$ . The calculation can be carried out analytically for weak inhomogeneity and the resulting density profile is given by:

$$\rho(\mathbf{r}) = \rho_0 \left[ 1 - \sum_i \Delta \rho(\mathbf{r} - \mathbf{R}_i) \right] \\ \Delta \rho(\mathbf{r}) = \int \frac{d\mathbf{q}}{(2\pi)^3} \exp(i\mathbf{q} \cdot \mathbf{r}) \frac{\beta v_{12}(q)}{1 + \rho_0 \beta v_{22}(q)} \quad (3)$$

where  $\rho_0$  is determined by imposing the constraint. By substituting Eq. (3) into Eq. (2) we obtain the two-body *effective* interaction experienced by particles ‘1’ due to the presence of particles ‘2’, which turns out to be globally attractive:

$$v_{\text{eff}}(q) = -\beta \rho_2 \frac{v_{12}(q)^2}{1 + \rho_2 \beta v_{22}(q)} \quad (4)$$

In the limit  $v_{22}(r) = 0$  and weak unlike interaction the procedure becomes exact and still predicts purely attractive interactions, which may drive the system to a collapse: a clearly unphysical result for a model with only *repulsive* terms ! Actually, many-body contributions to the effective interaction, which are obtained by including higher

orders in the minimization of the free energy but are usually disregarded, eventually stabilize the effective model. The analysis of this toy model suggests that many-particle terms in the effective hamiltonian are likely to play a crucial role in systems where particle overlap is not inhibited. This is also supported by the analysis brought forth in Ref.[15]. In that work, effective two-body forces in ternary gaussian mixtures were investigated by considering two big particles in a solvent of smaller particles at different compositions. Strongly attractive solvent-mediated interactions were found both in the special case of a pure solvent, and in the more general case where the solvent is itself a mixture of two species, when a dramatic increase in the effective interaction can occur as a consequence of preferential adsorption by the big particles. We observe that the result for  $v_{\text{eff}}$  reported in Eq. (4) of [15] for a pure solvent and very small solvent/solute size ratio coincides with that obtained in the same limit by Eq. (4) of the present work. Due to the above mentioned sensitivity of the phase diagram of mixtures on the form of the interactions, we conclude that many-body forces should be taken into account in deriving the effective hamiltonians, especially in soft core systems.

In summary, we have shown how a classic textbook subject like the thermodynamics of binary mixtures may present still open problems when applied to the case of complex fluids. In particular, attention has been focused on the sensitivity of the phase diagram to the strength of the unlike interaction and to the possibility of shaping the phase boundaries. Very soft effective potentials, like the GCM, are ideal systems for understanding the mechanisms underlying phase segregation in purely repulsive, athermal fluids.

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## Figure captions

**Figure 1.** Density-concentration coexistence regions of the symmetric HCY mixture for:  $T = 1.02$ ,  $\Delta = 0.6$  (left panel) and  $T = 1.02$ ,  $\Delta = 0.67$  (right panel). The quantities  $\rho$  and  $x$  are respectively the total density  $\rho = \rho_1 + \rho_2$  in reduced units and the relative concentration  $x = \rho_2/\rho$ . The gray scale is a measure of pressure (black: low pressure, white high pressure). Few tie lines are also shown.

**Figure 2.** Equimolar section of the density-temperature phase diagram of the symmetric HCY mixture for  $\Delta = 0.67$ .

**Figure 3.** Left panel: Phase boundaries of the symmetric gaussian core mixture in the density-concentration plane for  $\epsilon_{11} = 0.1$  (triangles),  $\epsilon_{11} = 1$  (squares),  $\epsilon_{11} = 2$  (circles) and  $\epsilon_{12} = 2\epsilon_{11}$ . Full symbols: HRT results; open symbols: HNC data; solid line: mean-field binodal. Here  $\rho = \rho_1 + \rho_2$ ,  $x = \rho_2/\rho$ , and  $\tilde{v}_{11}(0) = \pi^{3/2}\epsilon_{11}\sigma^3$ . Right panel: Two-body partial correlation functions of the same model in the case  $\epsilon_{11} = 0.1$  obtained via HRT (lines) for two thermodynamic states with  $x = 0.9$  and different densities:  $\rho\sigma^3 = 2$  (lower curves) and  $\rho\sigma^3 = 4$  (upper curves). Dots represent HNC data for  $\rho\sigma^3 = 2$ .

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